

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>TES-011-PCT</b>	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA416)	
International application No. <b>PCT/EP 03/05799</b>	International filing date (day/month/year) <b>03.06.2003</b>	Priority date (day/month/year) <b>04.06.2002</b>
International Patent Classification (IPC) or both national classification and IPC <b>C07C253/28</b>		
Applicant <b>TESSENDERLO CHEMIE S.A. et al.</b>		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 8 sheets, including this cover sheet.
 

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:
 

I    ☒ Basis of the opinion

II   ☐ Priority

III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability


IV   ☒ Lack of unity of invention

V    ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

VI   ☐ Certain documents cited

VII ☐ Certain defects in the international application

VIII ☐ Certain observations on the international application

Date of submission of the demand  <b>23.12.2003</b>	Date of completion of this report  <b>29.09.2004</b>
Name and mailing address of the international preliminary examining authority:   European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer  <b>Veefkind, V</b>  Telephone No. +31 70 340-1017



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP 03/05799**

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*):

**Description, Pages**

1-22 as originally filed

**Claims, Numbers**

1-29 received on 10.09.2004 with letter of 08.09.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
  - ☐ the language of publication of the international application (under Rule 48.3(b)).
  - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
  - ☐ filed together with the international application in computer readable form.
  - ☐ furnished subsequently to this Authority in written form.
  - ☐ furnished subsequently to this Authority in computer readable form.
  - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
  - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.
4. The amendments have resulted in the cancellation of:
- ☐ the description, pages:
  - ☐ the claims, Nos.:
  - ☐ the drawings, sheets:
5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/EP 03/05799

**III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application,

☒ claims Nos. 15-18,26-29

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (specify):

☒ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. 15-18,26-29 are so unclear that no meaningful opinion could be formed (*specify*):

**see separate sheet**

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for the said claims Nos.

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the Standard.

☐ the computer readable form has not been furnished or does not comply with the Standard.

**IV. Lack of unity of invention**

1. In response to the invitation to restrict or pay additional fees, the applicant has:

☐ restricted the claims.

☐ paid additional fees.

☐ paid additional fees under protest.

☐ neither restricted nor paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

☐ complied with.

☒ not complied with for the following reasons:

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP 03/05799**

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

- ☒ all parts.  
☐ the parts relating to claims Nos. .

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-14 (in part), 19-25
	No: Claims	
Inventive step (IS)	Yes: Claims	1-14 (in part), 20-25
	No: Claims	19
Industrial applicability (IA)	Yes: Claims	1-29
	No: Claims	

2. Citations and explanations

**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP 03/O 5799

Reference is made to the following documents:

- D1: ZHENG QIONG ET AL.: "A Direct Synthesis of Aromatic Nitriles from Methylaromatic Compounds by Ammonoxidation on DC-108 Catalyst" SYNTHETIC COMMUNICATIONS, vol. 29, no. 13, 1999, pages 2349-2353, XP008010117
- D2: CHEMICAL ABSTRACTS, vol. 132, no. 6, 7 February 2000 (2000-02-07), Columbus, Ohio, US; abstract no.: 65726e, ZHENG QIONG ET AL.: "Catalysts for Preparing 2,6-Dichlorobenzonitrile by Ammonia Oxidation Process" page 830 column 2 XP002219412
- D3: EP-A-0 141 228 (NIPPON KAYAKU KK) 15 May 1985 (1985-05-15)
- D4: DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; DIAO, XI-HUA ET AL: "Synthesis of 2,6- dichlorobenzonitrile by catalytic ammoxidation" XP002261463 retrieved from STN Database accession no. 134:224265
- D5: DATABASE WPI Section Ch, Week 199114 Derwent Publications Ltd., London, GB; Class B05, AN 1991-099164 XP002261464 & JP 03 044362 A (HODOGAYA CHEM IND CO LTD) 26 February 1991 (1991-02-26)
- D6: US-A-4 147 661 (HIGGINS RAYMOND ET AL) 3 April 1979 (1979-04-03)

**Re Item III**

Claim 15 is unclear (Article 6 PCT). It defines the catalyst in terms of two phases that must be present under "working conditions". Since the description makes clear that only one (common -see for example D1, page 2350-) phase is present before working conditions, the presence of the two phases under working conditions will thus depend on the exact "working conditions". Since these are not well defined, claim 15 lacks clarity, contrary to the requirements of Article 6 PCT. The use of this unclear parameter makes comparison with prior art, and therefore examination of novelty and inventive step, impossible. The use of these catalysts (claims 26-29) can neither be examined

**Re Item IV**

D3 discloses method of preparing halogenated benzonitriles by vapour phase ammoxidation using a three component catalysts (amongst others supported VPCrO, VPFeO, and VPCoO catalysts). The process can be carried out in a fixed bed or fluidized bed (see passages cited in the Search Report).

A) The contribution over prior art of independent claim 1 therefore lies in the presence of water vapour in the ammoxidation.

The contribution of independent claim 15, being a product by process claim, and the compositions per se being known from prior art, lies in the characterizing feature that under working conditions the catalyst mainly contains the two mentioned phases. It is clear from the description and Example 12 in the current application (see also Point VIII, below) that for some catalysts fulfilling the requirements of claim 15, in the presence of the preferred additive ethyl bromide, water vapour has a detrimental effect on the performance.

Since all these described catalysts presumably will exhibit the two phases of claim 15, the technical feature of having the two phases under reaction conditions (contribution over prior art of claim 15) cannot be said to correspond to the contribution over prior art of independent claim 1, i.e., the presence of water vapour.

Thus, the "special technical features" of claims 1 and 15 are not "same or corresponding" contrary to the requirements of Rule 13.2. PCT

This seems confirmed by the fact that the independent use-claim 26, which refers to claim 15, does not mention the presence of water vapour but rather relies on the specific catalyst characteristics.

B) The common problem underlying the invention, i.e, providing improved ammoxidation process and catalyst, is a common desire in the field and cannot serve as the general inventive concept required by Rule 13.1 PCT.

Consequently, these claims are not unitary according to Rule 13 PCT.

C) Thus, there are two groups of (alleged) inventions present:

- 1: claims 1-14, relating to an ammoxidation process in the presence of steam.
- 2: claims 15-29, relating to an ammoxidation catalyst, its preparation and its use.

#### **Re Item V**

1.1 For the general catalyst compositions of claim 1 (for example comprising Co or Fe), no example for the (beneficial) effect of water vapour is found. On the contrary, in the presence of ethyl bromide (preferred embodiment, see page 8, lines 5-6 and

specifically claimed in claim 14) the presence of steam is 'detrimental' to the catalytic performance of Co and Fe promoted catalysts (see page 8, lines 16-21). A beneficial effect of the presence of water vapour can be found only for CrVPO in Example 6 (Table 3). In the absence of examples for other catalyst compositions, and knowing from the application that under certain preferred circumstances for some three-component VMO catalysts the presence of water may be detrimental. It is therefore considered that claim 1 lacks support (Article 6 PCT) for the whole range of catalysts claimed.

1.2 Claims 15 and 19 are unclear because of the use of 'weakly oxidizing' atmosphere of  $O_2/N_2$ .

It is not clear how oxidizing a 'weakly oxidizing' atmosphere is, i.e., where - in clear technical features - the border between a 'weakly' oxidizing and a 'moderately' oxidizing atmosphere would be. Thus the scope of desired protection is unclear.

Claims 15 and 19, therefore, contravene Article 6 PCT.

### Novelty and Inventive Step (Article 33 PCT)

#### 2.1 First invention:

Insofar supported, i.e., for the supported three-component VMO catalyst with chromium (see above), the process of claim 1 seems novel and inventive.

None of the prior art documents disclose the presence of water vapour. The fact that it leads to a higher yield of desired product for CrVPO may be said to be unexpected and not derivable from the cited prior art documents or their combination.

#### 2.2 Second invention:

D6 (see passages cited in Search Report) discloses catalysts prepared by impregnating VMO catalysts with Mo. They may be supported. Calcination is done using air.

If 'weakly oxidizing' is interpreted (see point 1.2, above) as 'containing around 0.5% oxygen', claim 19 is novel.

The effect of the difference is not demonstrated. Since the catalyst in claim 15 mentions that the x in the catalyst composition is determined by the valencies of the other compounds, it must be assumed that although the oxygen concentration is smaller, more or less complete oxidation is achieved anyway.

It appears that claim 19 merely provides an alternative catalyst preparation

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/EP 03/05799

method. In the absence of a demonstrated effect of the preparation, the subject-matter of claim 19 cannot be accorded an inventive step, as the difference is one of the parameters the skilled person may vary in order to obtain essentially the same catalyst.

The steps recited in claim 20 cannot be said to be obvious steps in view of presently cited D1-D6. The subject-matter of claim 20, therefore, may presently be said to involve an inventive step (Article 33(3) PCT).

Dependent claims 21-25 also, insofar they relate to claim 20.



**Annex 1**  
**Amended claims (Clean version)**

1. A method for the preparation of halogenated benzonitriles by vapour phase ammoxidation of halogenated C<sub>1</sub> to C<sub>6</sub> alkyl benzenes, in the presence of water vapour, at a reaction temperature comprised in the range of 300 to 500 °C, using a three-component catalyst into a fixed bed reactor wherein said catalyst consists of a promoted VPO active phase provided on a carrier.
2. A method according to claim 1, wherein said reaction temperature is comprised in the range of 350 to 450 °C.
3. A method according to claim 1 or 2, wherein the residence time of the halogenated C<sub>1</sub> to C<sub>6</sub> alkyl benzene in said reactor is less than 10 seconds, preferably less than 8 seconds.
4. A method according to any of claims 1 to 3, wherein said halogenated C<sub>1</sub> to C<sub>6</sub> alkyl benzene is di- or tri-halogenated C<sub>1</sub> to C<sub>6</sub> alkyl benzene.
5. A method according to claim 4, wherein said di- or tri-halogenated C<sub>1</sub> to C<sub>6</sub> alkyl benzene is di-halogenated toluene.
6. A method according to claim 5, wherein said di-halogenated toluene is 2,6-dichlorotoluene.
7. A method according to any of claims 1 to 6, wherein said catalyst is provided on an Al<sub>2</sub>O<sub>3</sub> carrier.
8. A method according to any of claims 1 to 6, wherein said catalyst is provided on a TiO<sub>2</sub> carrier.
9. A method according to claim 8, wherein said TiO<sub>2</sub> carrier consists of the anatase phase.
10. A method according to any of claims 1 to 9, wherein said catalyst comprises a V<sub>1</sub>P<sub>a</sub>M<sub>b</sub>Al<sub>c</sub>O<sub>x</sub> or V<sub>1</sub>P<sub>a</sub>M<sub>b</sub>Ti<sub>c</sub>O<sub>x</sub> catalyst wherein M is chosen from the group comprising Cr, Fe, Co and Mo; a is 0.1 - 2.0; b is 0.002 - 1.0; c is 2.0 - 10.0, and x is determined by the valences of other component elements.
11. A method according to claim 10, wherein M is Co or Cr.
12. A method according to any of claims 1 to 11, whereby the catalyst is diluted with an inert medium in the ratio of 0.5 to 2.0 by weight with respect to the weight of said catalyst prior to its addition to the reactor.
13. A method according to claim 12 wherein said inert medium comprises corundum particles, porcelain beads, quartz beads, glass beads or the like.
14. A method according to any of claims 1 to 13, comprising the step of supplying a halogenated alkane to said reactor.
15. A supported and promoted VPO catalyst, suitable for use in a method according to any of claims 1 to 14, obtainable by a process comprising the steps of
  - preparing a bulk VPO precursor ;
  - impregnating said bulk VPO precursor with a promoter element in order to obtain a bulk promoted VPO precursor; and
  - adding a carrier to said bulk promoted VPO precursor,
  - and calcining the resultant mixture under a weakly oxidising atmosphere of O<sub>2</sub>/N<sub>2</sub> to obtain a supported and promoted VPO catalyst,
 whereby said catalyst is a V<sub>1</sub>P<sub>a</sub>M<sub>b</sub>Al<sub>c</sub>O<sub>x</sub> or V<sub>1</sub>P<sub>a</sub>M<sub>b</sub>Ti<sub>c</sub>O<sub>x</sub> catalyst wherein M is chosen from the group comprising Cr, Fe, Co and Mo; a is 0.1 - 2.0; b is 0.002 - 1.0; c is 2.0 - 10.0, and x is determined by the valences of other component elements, characterized in that the catalyst contains mainly two phases under working conditions a (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> phase and a (NH<sub>4</sub>)<sub>2</sub>(VO)<sub>3</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub> phase.
16. A catalyst according to claim 15, wherein said carrier is an Al<sub>2</sub>O<sub>3</sub> carrier.
17. A catalyst according to claim 15, wherein said carrier is a TiO<sub>2</sub> carrier.
18. A catalyst according to claim 17, wherein said TiO<sub>2</sub> carrier consists of the anatase phase.

19. A method for the preparation of a catalyst according to any of claims 15 to 18 comprising the steps of:
  - preparing a bulk VPO precursor;
  - impregnating said bulk VPO precursor with a promoter element in order to obtain a bulk promoted VPO precursor; and
  - adding a carrier to said bulk promoted VPO precursor,
  - and calcining the resultant mixture under a weakly oxidising atmosphere of  $O_2/N_2$  to obtain a supported and promoted VPO catalyst.
20. A method according to claim 19 comprising the steps of:
  - refluxing of a vanadium source in the presence of alcohols to obtain a solution containing reduced vanadium species;
  - adding of a phosphorus source and refluxing said solution in order to obtain a bulk VPO precursor;
  - impregnation of said bulk VPO precursor with an alcoholic or aqueous solution of a promoter element to obtain a bulk promoted VPO precursor;
  - mixing said bulk promoted VPO precursor with  $\gamma-Al_2O_3$  or  $TiO_2$  carrier powder; and shaping and calcining the resultant mixture to obtain a supported and promoted VPO catalyst.
21. A method according to claim 19 or 20, wherein said vanadium source is  $V_2O_5$  and said phosphorous source is  $o-H_3PO_4$ .
22. A method according to any of claims 19 to 21, wherein said promoter element comprises Cr, Fe, Co or Mo.
23. A method according to any of claims 19 to 22, wherein the ratio of said bulk promoted VPO precursor over said  $\gamma-Al_2O_3$  or  $TiO_2$  carrier powder is comprised in the range of 1:2 to 1:10, preferably 1:6.
24. A method according to any of claims 19 to 23, wherein the calcining step is performed at a temperature comprised in the range of 300 to 900°C for a period of 1 to 10 hours, under a calcining atmosphere.
25. A method according to any of claims 19 to 23, wherein the calcining step is performed at a temperature comprised in the range of 350 to 700°C for a period of 2 to 6 hours, under a calcining atmosphere of weak oxidising strength.
26. Use of a VPO catalyst according to any of claims 15 to 18 and prepared according to any of claims 20 to 26 in a vapour phase ammoxidation reaction.
27. Use of a VPO catalyst according to claim 26 in a vapour phase ammoxidation reaction according to any of claims 1 to 15.
28. Use of a VPO catalyst according to claim 27 for preparing 2,6-dichlorobenzonitrile from 2,6-dichlorotoluene in a vapour phase ammoxidation reaction.
29. Use of a VPO catalyst according to claim 28 in a vapour phase ammoxidation reaction of hetero aromatic hydrocarbons.